ACTIVITY REPORT

April 2001

Natural Gas & Oil Technology Partnership

bringing department of energy national laboratories capabilities to the petroleum industry

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Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November	**February, April, June, August, October, December**
Oil and Gas Recovery Technology Drilling, Completion, and Stimulation Technology Diagnostic and Imaging Technology	Upstream Environmental Technology Downstream Environmental Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: http://www.sandia.gov/ngotp/

Upstream Environmental Technology

Continuous Monitoring of Particulate Matter and Particulate Matter Precursor Emissions from Stationary Sources (Chevron and SNL)

Project is in close-out phase.

Development of an In-Well Oil/Water Separator for *In Situ* Recycling of Produced Water (Baker Hughes, Chevron, CINC, Oak Ridge Tool & Engineering, Phillips, REDA Pump, Texaco, Unocal, and ORNL)

No activity reported.

Stationary Source Emission Control Using Plasma-Assisted Catalysis (Cummins Engine, Edison Chouest Offshore, and LLNL)

Project is in close-out phase.

Reducing Chemical Use and Toxicity in Produced-Water Systems (BP Amoco, Rhorback Casasco Systems, and ANL)

Highlight:

- New software package tested in flow loop system with simulated produced water.

The objectives of this project are to (1) minimize the environmental discharge of hydrocarbons and treatment chemicals attributable to failures resulting from sustained localized pitting corrosion, (2) reduce the amount of toxic treatment chemicals used by field operators to prevent those failures, and (3) identify alternative treatments that reduce the use of toxic chemicals. One project approach has been to develop an online, real-time method to monitor sustained localized pitting corrosion so that treatment chemicals (e.g., biocides and chemical inhibitors) can be applied only where and when needed. In addition, field operators need to know whether pitting corrosion is from microbiologically influenced corrosion or other chemical corrosion mechanisms so that they can select either biocides or corrosion inhibitors for application. ANL has been developing an instrument that can be used by field operators to allow them to make such decisions. This instrument has also been used as a tool to evaluate less toxic treatment approaches.

The new user-friendly software package for automatic electrochemical noise (ECN) measurement and data interpretation was used to detect localized pitting corrosion in experiments using ANL's laboratory flow loop system. The experiments included evaluation of optimal electrode design in both microbially influenced corrosion (MIC) and chemical corrosion (CC) environments. The later experiments were designed to determine whether any distinguishable difference could be seen between the MIC and CC ECN signal patterns. The flow loop used to evaluate the optimal electrode design for the MIC experiment was filled with simulated produced water. Three ECN probes with electrodes of different degrees of surface roughness were inserted in the loop. Four metal coupons were also put into the loop to measure bacterial colonization by physical examination of the metal surface under an optical microscope. The CC flow loop was filled with a 1% NaCl solution. Two ECN probes with the modified electrodes were placed in the loop. Four coupons were also inserted in the CC loop to validate the general corrosion rate under CC attack.

The ECN measurement experiments in both flow loops were carried out for a total 700 hours. Only one interruption of the software occurred—at around 500 hours of measurement. A correction for this event was made to this data set.

The parametric indices of the corrosion process obtained from the analysis of the potential and current noise measurements were calculated and recorded every 10 minutes. The general corrosion rates of the ECN probes in both loops measured by weight loss corresponded well to the accumulated charges of corrosion current measured by the system. The optimal surface roughness of the ECN probes prepared by using a polishing slurry with particle sizes in the range of 0.3 mm to 1 mm was found to have the best sensitivity for detecting sustained localized pitting corrosion in a MIC environment. It was also found that the high-order statistical analysis of the ECN signal in the early stages of the corrosion process (i.e., during the initial 200 hours) on the probes might be used to differentiate MIC from CC attack. Specifically, the Kurtosis indices of the average potential and current of the ECN probes in the MIC environment have much higher values than the ECN probes in the CC environment (e.g., Kurtosis values of 50 versus 3 in the MIC and CC environments, respectively). This phenomenon may occur because the Kurtosis analysis is used to characterize the relative peaks or flatness of a distribution as compared to a normal distribution of the signal. The colonization of bacteria on the metal surface during the MIC attack may create much more volatile noise signals as created by the relatively smooth surface coverage of corrosion products on the metal surface in the CC environment. In the later stages of corrosion, when the bacteria colonization stopped (indicated by the microscopic analysis of the metal coupons), the Kurtosis values of ECN probes in the MIC flow loop were close to the values of the probes in the CC flow loop. Validation of this basic finding was accomplished by reanalyzing the large number of ECN signal records that were created in ANL's previous laboratory experiments. Modification of the software package to incorporate the *in situ* Kurtosis analysis is now being carried out.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

Highlights:

- CRADA placed.
- Finalized immobilization criteria of biomass for site application.

Preparation for the field demonstration continues. The University of Tulsa continues to iterate design criteria with a fabricator in Tulsa, OK, for final cost estimation of equipment for deployment. Results are expected in the third week of May.

The publication, "Characterization of a novel biocatalyst system for sulfide oxidation," was made available on the Internet as a "As Soon As Possible" publication (http://pubs.acs.org/CHECKCCIP-989253836/isubscribe/journals/bipret/jtext.cgi?bipret/asap/html/ bp0100169.html) The paper was written by C. McComas, and K.L. Sublette, both of the University Tulsa; G.E. Jenneman, of Phillips Petroleum; and G.A. Bala, of INEEL. Availability on the Internet proceeds printed distribution of *Biotechnology Progress*.

A cooperative research and development agreement was placed with Phillips Petroleum.

Characterization of Soluble Organics in Petroleum Waste Water

(Chevron, Marathon, Phillips, Shell, Statoil, and ORNL)

Highlight:

- The contribution of low molecular weight acids (C_1–C_6) to total WSO content in produced waters was determined.

The objective of this project is to characterize and evaluate water solubles aimed at reducing future production of these contaminants in produced water. ORNL is currently identifying water soluble organics (WSO) in produced water derived from Gulf of Mexico (GOM) crude oil/brine contacts. A number of contact experiments have been performed to determine the influence of the percent water/oil cut, pH, salinity, temperature and pressure on the quantity of extractable organics found in GOM brine.

The contribution of low molecular weight acids (C_1–C_6) to total WSO content in produced waters has been determined. At ambient temperature and

pressure the concentration of organic acids is nearly equivalent to that of petroleum hydrocarbon content. Acetic acid is most prevalent, followed by proprionic and formic acids. Acid content decreases as the alkalinity of GOM brine increases.

Polar organic compounds comprise the majority of WSO found in treated brine. Total petroleum hydrocarbons are present in the concentration range of 20–30 ppm. The mass of WSO derived from small organic acids (C_1–C_6) is present at a level of less than 30 ppm. Organic acids identified by ion chromatography include formic, acetic, and proprionic acids, with acetic acid making up the bulk of the acid mass. Acid levels were found to decrease as the brine simulant became more alkaline—a trend opposite that observed for hydrocarbon content. Both salinity and temperature slightly elevate organic acid concentration, particularly that of acetic acid. Less than 5 percent total acid in produced water is recovered with a methylene chloride extraction; less than 1 percent organic acids are recovered in a hexane extraction. For 30 ppm total acid present in produced water, it is estimated that total petroleum hydrocarbon content would be overestimated by less than 2 ppm if methylene chloride is used to extract WSO from produced water and by 0.5 ppm if hexane is used for solvent extraction. Assuming a constant distribution coefficient, overestimation of WSO content would then increase linearly relative to total acid concentration in the produced water.

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, Chevron, Exxon, Gas Technology Institute, Texaco, Unocal, LBNL, ORNL, and LLNL)

Highlights:

- Reviewed computer programs for use in ecological modeling.
- Reviewed additional models and critical patch-size data from literature.

This was a slow period for the project as researchers await late springtime or early summer for a visit to the case study site, the Tallgrass Prairie Preserve in Osage County. ORNL began to consider two models for potential use in this project: Program to Assist in Tracking Critical Habitat (PATCH), written by Nathan Schumaker at EPA Corvallis, OR (Schumaker 1995, 1998) and Self-Avoiding Walkers (SAW), written by Robert Gardner of the Appalachian Ecology Lab and Eric Gustafson of the U.S. Forest Service. Project researchers are also evaluating additional models identified in LLNL's literature review of models potentially relevant to animals in a patchy, terrestrial landscape. It is not yet clear whether these models will be utilized to develop exclusion criteria (excluding E&P sites from formal risk assessments) or mitigation recommendations for E&P sites. We are also evaluating data collected by LLNL on critical patch size and habitat use. These data will be used in preparing a modeling approach for the project and selecting modeling endpoints. LLNL continues to make progress in staging the web site to house the project Geographic Information System.

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

The paper describing an early application of exercising the uncertainty framework was completed. This framework application is associated with a corroborative analysis that evaluates the accuracy of an important model improvement concerned with the photochemistry. The paper has been submitted for publication.

Work began on an application to evaluate uncertainties in modeled hydrocarbon concentrations as a function of space and time. The hydrocarbons of concern are ozone precursors. The hydrocarbons will be estimated using the CMAQ model, which is the new EPA air quality model, and two chemical mechanisms: CB-IV and SAPRAQ-99. The emissions inventory to be used is

the California Air Resouces Board (CARB) revision of the 1990 inventory and the monitored data are from the 1990 San Joaquin Valley Study.

Comprehensive review continued on certain elements of the uncertainty framework. Work on a paper describing approaches to evaluating model uncertainty is ongoing.

The project's principal investigator and a LBNL scientist met with CARB modelers in Sacramento.

Remote Sensing for Environmental Baselining and Monitoring

(Chevron, UC-Davis, and ORNL)

Highlight:

- Acquired spectroradiometer.
- Acquiring remote hperspectral data and software.
- Attended conference.

ORNL has received a 512-band field FieldSpec Pro spectroradiometer from Analytical Spectral Devices. Project researchers are learning how to collect data with the system and writing software to analyze the datasets.

Hyperspectral data will be collected at the oil spill site at the Jornada Experimental Range near Las Cruces, NM, when we receive our funding for FY01. ORNL has made contacts to acquire remote hyperspectral data for the Jornada site and to acquire software for analyzing hyperspectral data. ORNL is acquiring soil-sample data for the site from Chevron.

Two ORNL staff members attended the American Society for Photogrammetry and Remote Sensing annual meeting. A one-day workshop provided an introduction to state-of-the-art approaches for hyperspectral analysis. Several sessions focused on the use of hyperspectral analysis methods to evaluate the condition of various species of plants.

Downstream Environmental Technology

Bioprocessing of High-Sulfur Crudes via Application of Critical Fluid Biocatalysts

(Texaco, UOP, and INEEL)

Highlights:

- Enzymatic reactions conducted as base comparisons.
- CRADA placed with UOP.

Work exploring biocatalysis in organized media, including reverse micelles, microemulsions, and emulsions continued in April. Previous work focused on the perfluoropolyether (PFPE) surfactant, which does not require a co-surfactant when used in supercritical carbon dioxide. The experimental effort using supercritical carbon dioxide found no conversion of dibenzothiophene (DBT) by hemoglobin (Hb) to the oxidation products.

Initial microemulsion experiments in supercritical fluids showed no reaction. Control experiments indicated that hydrogen peroxide may not have been delivered to the high-pressure view cell reactor, and that there were problems with the temperature control system. System modifications were made, and control experiments demonstrated that the modifications fixed the known issues.

Hb catalyzed oxidation of DBT in supercritical carbon dioxide microemulsions was performed at 40°C and 3050–3100 psi. The reaction was run in three different buffers. The 1 M buffers included potassium phosphate (pH 7), Tricine (pH 8.5), and sodium acetate (pH 6.83). No product was formed in these reactions. Different quantities of Hb and different addition methods were also explored.

It was hypothesized that interactions between the buffer and the carbon dioxide may be inhibiting the Hb. Control experiments were performed exploring the Hb oxidation of DBT in liquid buffer exposed to supercritical carbon dioxide or ethane. Experiments with supercritical carbon dioxide demonstrated that less than 1 percent product yield at the highest buffer concentration of 1 M potassium phosphate, and no measurable product yield at lower

buffer concentrations. In contrast, reaction in 0.1 M liquid buffers exposed to supercritical ethane produced product yields of approximately 65 percent. These results suggest that carbon dioxide increases acidity dramatically hindering transformation. Work in organized media will now focus on ethane as the supercritical fluid.

Several control experiments were performed in April. One set of control experiments demonstrated some loss of sample due to transferring of stock solutions, but experiments in the high-pressure reactor using supercritical fluids resulted in relatively good recoveries. Control experiments conducted in glassware determined that reaction storage at -180ºC followed by warm-up to room temperature for a few hours restored the protein activity. Immediate work-up of reaction products is required. Acetate-phosphate buffer at 0.1 M concentrations (pH 5.2) was found to be the preferred buffer. At 30ºC, the product was mainly the DBT sulfoxide, but both sulfoxide and sulfone were produced at 40ºC. Given the small size loop (5 ml) used to load hydrogen peroxide to the high-pressure cell, external reactions were conducted in small glassware. Transformation was detected by gas chromatograph regardless if 5 or 20 ml hydrogen peroxide was added (maintaining the final concentration).

Biological Upgrading of Heavy Oils for Viscosity Reduction

(BP Amoco, Chevron, EPRI Chemicals, Natural Gas Center, Texaco, and LBNL)

Highlights:

- Evaluation of 11 strains completed.
- Study results presented at the American Chemical Society meeting.

The objective of this project is to develop novel biocatalytic agents for the terminal oxidation of alkanes in mixtures. Biocatalytic agents that will oxidize longer chain (C_8 and greater) alkanes without oxidizing gasoline range alkanes (less than C_8) are particularly desirable. These biocatalytic agents will be evaluated for use in the biological upgrading of crude oil. Project researchers currently have approximately 50 pure bacterial cultures capable of oxidizing alkanes. These cultures are being systematically evaluated for their phylogenic, genetic and physiological diversity.

Research over the last months has focused on completing evaluations of 11 strains selected as priorities from the complete culture collection. Each of these strains has been screened for fatty acid methyl ester (FAME) profile. Genomic DNA has been isolated for 16s rDNA analysis. These strains have been tested for homology with known *alkB* gene sequences and the results of the genetic analysis have been correlated with physiological tests measuring alkane oxidation profiles.

The results of evaluation have demonstrated that the majority of the bacteria in the project collection have homology with known *alkB* gene sequences. This sequence is correlated with the ability to transform low-molecular weight (C_8 and less) alkanes. Two strains that only oxidize select, longer chain alkanes do not show homology with *alkB* genes by project protocols. The lack of homology with *alkB* suggests that these strains may contain novel enzymes. One strain has a high specificity in target substrates and is considered of high potential value as a biocatalytic agent.

The results of this study were presented at the national meeting of the American Chemical Society in San Diego on April 5. Further research is focusing on the evaluation of the most promising strains.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, Chevron, Shell, and BNL)

No activity reported.

Enzymatic Upgrading of Heavy Crudes via Partial Oxidation or Conversion of PAHs

(Chevron, Phillips, Texaco, ORNL, and INEEL)

No activity reported.

A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

(Aerosol Dynamics, Envair, Western States Petroleum Association, and LBNL)

Highlights:

- Filter samples from intensive measurement periods analyzed.
- Continued model development.
- Began documenting results for journal publication.

Work continued on analysis of the filter samples from the project's intensive measurement periods. Analysis of total particulate mass and the total particulate mass of sulfate, nitrate, and ammonia and carbon was completed. All the carbon samples were analyzed, except for the few samples being reserved for more in-depth analysis. Quality control procedures and pre-analysis methodology verification were completed for the analysis of ionic species on the coated filters. Analysis of these filters was initiated and continues.

The main areas of current model enhancement are development of an ammonia-nitric acid mechanism into the model; analysis of model sensitivity to co-varying parameters, such as peak concentrations which may occur during periods of high air infiltration; and incorporation of the LBNL infiltration model to predict infiltration rate based on meteorology.

Work has begun on two journal manuscripts describing project results. The first manuscript describes the intensive experiments performed at the Clovis house, presents results from these experiments, and describes the most important findings. The second manuscript describes transient experiments performed at both the Clovis and Richmond sites, reports conclusions regarding penetration into and deposition within homes, and analyzes the effect of penetration and deposition losses on indoor particle concentrations.

The Principal Investigator and the two project leaders presented an overview of the study and their initial findings to the Technical Committee of the California Regional Particulate Air Quality Study at the California EPA in April.

Real-Time Characterization of Metals in Gas and Aerosol Phases

(BP Amoco, Equilon, Marathon, Phillips, Shell, Eastman Chemicals, and ORNL)

No activity reported.

Partnership Office

Clearly, the FY02 budget will have impact on the Partnership. The nature and extent of the impact, although major, is not yet determined. The laboratory and industry participants will await DOE guidance about how to proceed, as the DOE addresses the challenges this summer.

The Partnership is preparing this month to start the approved projects for FY01. This new year is particularly exciting because ten new projects will be initiated. We are working to finalize the scope of these projects and to complete the associated technology transfer.